

PATENT SPECIFICATION

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(54) PROCESS FOR THE OXIDATION OF OLEFINS TO
 ALDEHYDES AND ACIDS

(71) We, THE STANDARD OIL
 COMPANY, a corporation organised under
 the laws of the State of Ohio, United States
 of America, of Midland Building, Cleveland,
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 hereby declare the invention, for which we
 pray that a patent may be granted to us, and
 the method by which it is to be performed,
 to be particularly described in and by the fol-
 lowing statement:—

The present invention relates to a process
 for the conversion of propylene and/or iso-
 butylene to acrolein and/or methacrolein
 and/or acrylic acid and/or methacrylic acid.

The present invention provides a process
 for the conversion of propylene or isobutylene
 or a mixture thereof to acrolein and/or meth-
 acrolein and/or acrylic acid and/or meth-
 acrylic acid, which process comprises contact-
 ing propylene and/or isobutylene with mole-
 cular oxygen in the presence of a catalyst com-
 prising a composition having the empirical
 formula:



wherein A is an alkali metal, B is phosphorus
 and/or arsenic, C is at least one element selec-
 ted from Group II A and Group II B of the
 Periodic Table, a is a number from 0 to less
 than 0.1, b is a number from 0 to 3, c is a num-
 ber from 0.1 to 10, d and e each is a number
 from 0.1 to 6, f is a number from 8 to 16 and
 x is a number determined by the valence re-
 quirements of the elements present other than
 oxygen, said contacting being carried out in
 the vapour phase at a temperature of from
 500° to 900° F. and at a pressure of from
 0.5 to 5 atmospheres.

The catalyst used in the process according
 to the invention has a number of advantages

that contribute greatly to the efficient and
 economic operation of the process. The cata-
 lyst has excellent redox stability under the
 reaction conditions of the process. Further-
 more, such a catalyst exhibits high activity
 and selectivity in the conversion of olefins to
 the desired olefin oxidation products. Since
 the bismuth content of the catalyst dictates to
 a large extent the cost of the components from
 which the catalyst is prepared, such cost may
 be kept low. This low cost of catalytic in-
 gredients coupled with the ease of catalyst pre-
 paration make this catalyst very attractive
 from an economic standpoint.

The high activity of such a catalyst having
 a low bismuth content is surprising in view of
 the conversions reported in U.S. Patent No.
 2,941,007, which describes a process for the
 production of unsaturated aldehydes and
 ketones from alpha-olefins in the presence of
 a catalyst consisting of bismuth molybdate or
 bismuth phosphomolybdate, and in view of
 the conversions reported in U.S. Patent No.
 3,171,859 which describes a process for the
 production of unsaturated aldehydes from ole-
 fins in the presence of a catalyst comprising
 the oxides of iron, bismuth, phosphorus and
 molybdenum.

A further advantage of the process accord-
 ing to the present invention is that propylene
 and/or isobutylene may be converted directly
 to acrylic acid and/or methacrylic acid in high
 yield if the reaction conditions are chosen
 appropriately; in this connection, the commer-
 cial investment in plant required for convert-
 ing, for example, propylene to acrylic acid is
 considerably lower for a single-step process
 than for a two-step process.

The propylene or isobutylene, or a mixture
 thereof, may be used when in admixture with
 a paraffinic hydrocarbon, e.g. selected from

ethane, propane, butane and pentane; for example, a propylene-propane mixture may constitute the feed. Ordinary refinery streams may thus be used without special preparation. Likewise, diluents such as nitrogen and the oxides of carbon may be present in the reaction mixture without deleterious effect.

Any source of molecular oxygen may be employed. For economic reasons, however, it is preferred that air be employed as the source of oxygen. From a purely technical viewpoint, the use of relatively pure molecular oxygen will give equivalent results. The molecular oxygen is supplied to the reaction vessel in an amount to provide an oxygen:olefin molar ratio of preferably from 5:1 to 0.5:1, a ratio of from 1:1 to 3:1 being especially preferred.

We have found in some cases that the yield of and selectivity towards unsaturated aldehydes and/or acids is improved by the inclusion of water in the reactants fed to the reaction vessel. However, the use of such added water is not essential inasmuch as water is formed in the course of the reaction. If such addition of water is employed, in general, it is used to provide an added water:olefin molar ratio of from 0.25:1 to 20:1, a ratio of from 1:1 to 4:1 being particularly desirable.

The reaction is carried out at a temperature of from 500 to 900° F, preferably of from 550 to 750° F, at a pressure of from 0.5 to 5 atmospheres.

The apparent contact time between the reactants and the catalyst is not critical and may range from 0.1 to 50 seconds. The optimum contact time will, of course, depend upon the olefin reactant but, in general, a contact time of from 1 to 15 seconds is preferred.

The formation of unsaturated carboxylic acids is favoured by higher reaction temperatures, higher ratios of oxygen to olefin and longer contact times, the converse being true for the formation of unsaturated aldehydes. When maximum conversion to unsaturated acids is desired, it is advantageous to recycle the formed unsaturated aldehyde. The recycled unsaturated aldehyde can be combined with a recycle of steam and/or unreacted olefin.

Any apparatus of the type suitable for carrying out oxidation reactions in the vapour phase may be employed. The process may be conducted either continuously or intermittently. The reactor may employ a fixed-bed of large particulate or pelleted catalyst or, alternatively, a so-called "fluidized" bed of catalyst. The reactor may contain a plurality of perforated trays stacked horizontally throughout the length of the column, as described in U.S. Patent No. 3,230,246, or may comprise, for fluidized bed operation, an open column.

The reactor may be brought to the reaction temperature before or after the introduction of the reaction feed mixture. However, in a large scale operation it is preferred to carry

out the process in a continuous manner with recycling of the unreacted olefin.

Although the catalyst is redox stable, regeneration or reactivation of the catalyst may be accomplished, if necessary, by contacting the catalyst with air at an elevated temperature.

The products of the reaction may be recovered by methods known to those skilled in the art. One such method involves scrubbing the effluent gases from the reactor with cold water or an appropriate solvent to remove the products of the reaction. The ultimate recovery of the products may be accomplished by conventional means. The efficiency of a scrubbing operation employing water as the scrubbing agent may be improved by incorporating a suitable wetting agent in the water. In the case where the molecular oxygen is supplied in the form of molecular oxygen, the reaction product remaining after the removal of the carbonyl and carboxylic acid compounds may be treated to remove carbon dioxide and water, the residue of the product containing the unreacted olefin and oxygen being recycled through the reactor. In the case where air is employed as the source of molecular oxygen, the reaction product remaining after the removal of the carbonyl and carboxylic acid compounds may be scrubbed with a non-polar solvent, e.g. a hydrocarbon fraction, in order to recover unreacted olefin, the remaining gas being discarded. A suitable inhibitor to prevent polymerization of the unsaturated reaction products during the recovery steps may be added, if desired.

Referring to the catalyst, a preferred catalyst composition is one in which A is potassium, C is a Group II A metal, and the composition has an empirical formula such that a is a number from 0 to 0.09, b is a number from 0 to 1, c is a number from 0.1 to 7, d and e each is a number from 1 to 4 and f is 12. Most preferred is a catalyst composition wherein the Group II metal is magnesium.

The catalyst composition may be prepared by any of the numerous methods of catalyst preparation which are known to those skilled in the art. For example, the catalyst composition may be manufactured by co-precipitating the various ingredients. The co-precipitated material may either be dried and ground to an appropriate size, or may be slurried and spray-dried in accordance with conventional techniques. The catalyst composition may be extruded as pellets or formed into spheres in oil as is well-known in the art. Alternatively, the components from which the catalyst composition is to be prepared may either be mixed with support material in the form of the slurry followed by drying or may be impregnated on support material, e.g. silica.

As starting material for the alkali metal component there may be used an alkali metal oxide or any alkali metal salt which, upon cal-

cination, yields an alkali metal oxide. Preferred salts are the nitrates which are readily available and easily soluble.

5 As starting material for the bismuth component there may be used a bismuth oxide or any bismuth salt which, upon calcination, yields a bismuth oxide. The preferred salts are water-soluble salts which are easily dispersible with the other catalyst starting materials and which
10 form stable oxides upon heating. The most preferred salt is bismuth nitrate.

As starting material for the iron component there may be used any compound of iron which, upon calcination, yields an oxide of iron. As with the other elements, water-soluble
15 salts are preferred for the ease with which they may be uniformly dispersed with the other catalyst starting materials. The most preferred salt is ferric nitrate.

20 As starting material for the Group II element component there may be used any compound of a Group II element analogous to the compounds of iron mentioned above; an insoluble carbonate or hydroxide which
25 upon heating yields the corresponding oxide may be used; however, as mentioned above, soluble salts are preferred.

As starting material for the molybdenum component there may be used any molybdenum
30 oxide, e.g. the dioxide, trioxide, pentoxide or sesquioxide, or, preferably, a hydrolyzable or decomposable molybdenum salt, e.g. a molybdenum halide. A preferred starting material is ammonium heptamolybdate.

35 Such starting materials may be derived from the metal which is oxidized with an oxidizing acid such as nitric acid to provide the corresponding nitrate which is used in the preparation
40 of the catalyst. Generally, however, the nitrates are readily available and form a very convenient starting material.

As starting material for the arsenic component there may be used orthoarsenic acid.

45 As starting material for the phosphorus component there may be used an alkali metal salt, an alkaline earth metal salt or an ammonium salt of phosphoric acid. A preferred starting material is phosphoric acid.

50 Starting materials other than those mentioned hereinabove may be used, particularly when the preferred starting materials mentioned hereinabove are unsuited to the economics of large-scale manufacture. In general,
55 any compound containing a desired catalyst component may be used provided that it yields an oxide upon heating to a temperature within the range disclosed hereinafter.

60 The composition can be employed without support material and as such displays excellent activity. Alternatively, the composition can also be combined with support material which preferably constitutes from 10 to 90
65 weight percent of the catalyst. Suitable support materials are materials which are stable under the reaction conditions to be encoun-

tered in the use of the catalyst, for example silica, alumina (in particular, "Alundum" (Registered Trade Mark)), zirconia, titania, silicon carbide, alumina-silica, inorganic phosphates such as aluminium phosphate, silicates, aluminates, borates, carbonates, pumice and montmorillonite.

A particularly attrition-resistant form of catalyst may be prepared by adding the support material to the catalyst in two stages, for example by heating a mixture containing support material and components which will provide said composition upon heat-treating, said mixture containing support material in an amount constituting up to 60 percent by weight of the support material which is to be included in the catalyst and said heating being effected at a temperature of from 1000 to 2000° F. in an oxidising atmosphere; reducing the resulting material to a fine powder; mixing the powder with an aqueous slurry of the remaining support material; drying the resulting mixture; and calcining the dried mixture at a temperature of from 750 to 2000° F. A more detailed description of the preparation of an attrition-resistant catalyst is given in the Examples. Generally, prior to use the catalyst is dried and heated at a temperature of from 500 to 1800° F., preferably from 900 to 1300° F., for from one to twenty-four hours. If the activity then is not sufficient, the catalyst can be further heated at a temperature above 1000° F. but below a temperature deleterious to the catalyst.

In general, activation of the catalyst is achieved in less time at the higher temperatures. The sufficiency of activation at any given set of conditions is ascertained by a spot test of a sample of the material for catalytic activity. Activation is best carried out in an open chamber, permitting circulation of air or oxygen, so that any oxygen consumed can be replaced.

Prior to use, the catalyst may be treated with a reducing agent in the presence of a limited amount of air at a temperature of from 500 to 1000° F.

The invention is illustrated by the following Examples 1 to 16 of which Examples 1 to 13 relate to the conversion of propylene to acrolein and acrylic acid and Examples 14 and 15 relate to the conversion of isobutylene to methacrolein and methacrylic acid (Examples 1 to 4 and 14 being comparative examples lying outside the scope of the invention and Examples 5 to 13 and 15 exemplifying the process according to the invention) and Example 16 relates to the preparation of a catalyst.

Examples 1—15.

In each example, a standard reactor containing about 5 cc of catalyst was employed, a fixed bed of catalyst having a particle size of 20 to 35 Tyler screen mesh being used in

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- Examples 1 to 9 and 11 to 15 and a fluidized bed of catalyst having a particle size of 50 to 80 Tyler screen mesh being used in Example 10. Olefin, air and steam were metered to the reactor with rotameters in amounts to provide an olefin:air:steam molar ratio of 1:11:4. The reaction temperature and contact time for each example were as specified in Tables I and II. Reaction was carried out for 30 minutes after a 15 minute pre-run period. The reaction products were recovered by scrubbing the effluent gas from the reactor with water and then were analyzed by gas chromatography. The results for each example are set forth in Tables I and II, the term "yield", as used therein, being defined as follows:

$$\text{yield, \%} = \frac{\text{Moles of stated product obtained}}{\text{Moles of olefin fed}} \times 100$$

- The composition of the catalyst employed in each example is set forth in Tables I and II; further details relating to the catalysts and their method of preparation are given below.
- The catalyst employed in Examples 1 and 2 was prepared according to the procedure described in U.S. Patent No. 2,941,007. The catalyst employed in Examples 3, 4 and 14 was prepared according to the procedure described in U.S. Patent No. 3,171,859.
- The catalysts employed in Examples 5, 7, 8, 9, 11, 12 and 13 were prepared, using the appropriate starting materials, by a procedure essentially the same as the following procedure which relates specifically to the preparation of a catalyst containing 80 wt. % of a composition having the empirical formula
- $$\text{K}_{0.07}\text{Mg}_{4.5}\text{Fe}_4\text{Bi}_2\text{P}_{0.5}\text{Mo}_{12}\text{O}_{81}$$
- and 20 wt. % SiO_2 . 70.6 grams $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved in water with a minimum amount of heating. To the resulting solution were added, in succession with stirring, 1.9 grams H_3PO_4 (85 wt. %) and 76.7 grams of colloidal silica sol (Ludox AS; "Ludox" is a Registered Trade Mark) containing 30 wt. % silica. The resulting mixture was stirred for 15 minutes at room temperature. An aqueous solution containing 53.7 grams $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to the stirred mixture followed by the successive addition of 38.5 grams $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.23 grams KNO_3 and an aqueous solution containing 32.4 grams $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 8 cc of concentrated HNO_3 (68 wt. %). The resulting slurry was heated with constant stirring until a gel formed. The gel was dried at approximately 270° F. The resulting material was heated initially at 600° F. for 5 hours and then at 1020° F. for 20 hours, and thereafter was sized to 20—35 Tyler screen mesh.
- The catalyst employed in Examples 6 and 15, which catalyst was an unsupported catalyst consisting of a composition having the empirical formula $\text{Mg}_{4.5}\text{Fe}_4\text{Bi}_2\text{P}_{0.5}\text{Mo}_{12}\text{O}_{81}$ was prepared by a similar procedure except that additions of colloidal silica sol and of potassium nitrate were omitted and the bismuth nitrate solution contained only 6 cc of concentrated nitric acid.
- The catalyst employed in Example 10, which catalyst was an attrition-resistant catalyst containing 60 wt. % of a composition having the empirical formula
- $$\text{Mg}_{4.5}\text{Fe}_4\text{Bi}_2\text{P}_{0.5}\text{Mo}_{12}\text{O}_{81}$$
- and 40 wt. % SiO_2 , was prepared as follows: 706 grams $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved in 570 cc water, using minimum heating. The resulting solution was blended with 19 grams 85% H_3PO_4 . To the resulting solution were added 767 grams of silica sol (Ludox AS) containing 30 wt. % silica, followed by the successive addition of an aqueous solution containing 537 grams $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 250 cc water and an aqueous solution containing 385 grams $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 190 cc water. Whilst stirring the resulting mixture vigorously, a solution prepared from 324 grams $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 30 cc 68% HNO_3 and 380 cc water was added. The resulting slurry was heated with stirring until a non-fluid cake was obtained. The cake was dried by heating at 600° F. for 5 hours. The dried cake was pulverized mechanically. 1000 grams of the resulting powder were blended with 1125 grams of silica sol (Ludox AS) containing 30 wt. % silica and sufficient water to provide a slurry containing 40 wt. % solids. The slurry was ball-milled in a porcelain ball-mill for 20 hours and then spray-dried in a 4½ foot diameter Bowen spray-drier with an inlet temperature of 550° F. and an outlet temperature of 350° F. The microspheroidal product from the spray-drier was placed in a furnace at 280° F. The temperature of the furnace was raised to 600° F. over a period of one hour and maintained at 600° F. for three hours. The material was calcined at 1100° F. for 15 hours prior to use in the fluid bed reactor.

TABLE I
CONVERSION OF PROPYLENE TO ACRYLEIN AND ACRYLIC ACID

Example	Catalyst Composition (by weight)	React. Temp. (°F)	Cont. Time (Sec)	Per Pass Acrolein	Conversion (%) to: Acrylic Acid
1.	50%-Bi ₉ P ₁₂ O ₅₂ -50% SiO ₂	680	2.5	22.8	2.9
2.	ditto	680	5.0	35.6	3.5
3.	50%-Fe _{4.5} Bi _{4.5} P ₁₂ O ₅₂ -50% SiO ₂	605	2.5	22.0	3.9
4.	ditto	680	5.0	48.5	6.8
5.	80%-Mg _{6.5} Fe ₃ Bi ₁ P _{0.5} Mo ₁₂ O ₄₉ -20% SiO ₂	680	5.0	64.4	10.6
6.	100%-Mg _{4.5} Fe ₄ Bi ₂ P _{0.5} Mo ₁₂ O ₅₁	680	5.0	78.3	5.7
7.	80%-Mg _{4.5} Fe ₄ Bi ₂ P _{0.5} Mo ₁₂ O ₅₁ -20% SiO ₂	605	2.5	67.3	7.8
8.	ditto	680	2.5	54.3	17.2
9.	ditto	680	5.0	51.2	20.6
10.	60%-Mg _{4.5} Fe ₄ Bi ₂ P _{0.5} Mo ₁₂ O ₅₁ -40% SiO ₂	605	2.5	64.2	8.6
11.	80%-K _{0.07} Mg _{4.5} Fe ₄ Bi ₂ P _{0.5} Mo ₁₂ O ₅₁ -20% SiO ₂	680	5.0	71.1	12.1
12.	80%-Mg _{4.5} Fe ₄ Bi ₂ As _{0.5} Mo ₁₂ O ₅₁ -20% SiO ₂	680	2.5	68.3	10.2
13.	80%-Mg _{4.5} Fe ₄ Bi ₂ Mo ₁₂ O ₅₀ -20% SiO ₂	680	2.5	65.9	5.3

TABLE II
CONVERSION OF ISOBUTYLENE TO METHACROLEIN AND METHACRYLIC ACID

Reaction Temp: 680°F

Contact Time: 2.5 seconds

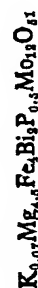
Example	Catalyst Composition (by weight)	Per Pass Conversion (%) to:	
		Methacrolein	Methacrylic acid
14.	50%-Fe _{4.5} Bi _{4.5} P _{1.2} Mo ₁₂ O ₅₂ -50% SiO ₂	28.6	4.0
15.	100%-Mg _{4.5} Fe ₄ Bi ₂ P _{0.5} Mo ₁₂ O ₅₁	48.5	4.8

The results set forth in Tables I and II show that the per pass yields of acrolein, acrylic acid, methacrolein and methacrylic acid obtained by operating according to the process of the invention are substantially higher than those obtained by operating according to prior art processes wherein known catalysts are used.

Furthermore, comparable results are given for a process employing a fixed bed of pelleted catalyst and for a process employing a fluidized bed of fluid-type catalyst.

Example 16.

A catalyst containing 80 wt. % of a composition having the empirical formula



and 20 wt. % SiO₂ was prepared as follows. 212 grams (NH₄)₆Mo₁₂O₅₄·4H₂O were dissolved in water with a minimum amount of heating. 5.7 grams H₃PO₄ (85 wt. %) and 230 grams of colloidal silica sol (Ludox AS) containing 30 wt. % silica were added in succession with stirring to the resulting mixture. An aqueous solution containing 161 grams Fe(NO₃)₃·9H₂O was added to the stirred mixture followed by the successive addition of 115.5 grams Mg(NO₃)₂·6H₂O and an aqueous solution containing 0.69 grams KNO₃. Whilst stirring the resulting mixture vigorously, an aqueous solution containing 97.2 grams Bi(NO₃)₃·5H₂O and 9 cc of concentrated HNO₃ (68 wt. %) was added. The resulting slurry was stirred continuously for

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about 15 minutes and then spray-dried. The powder obtained from the spray-drier was further dried in an oven at 230° F. for 16 hours. The resulting dry powder was intimately mixed with 1 wt. % graphite and compacted into $\frac{1}{8} \times \frac{1}{8}$ pellets using a conventional pelleting machine. The pellets were heated for 5 hours at 450° F. to decompose the nitrates and then calcined for 20 hours at 1020° F.

WHAT WE CLAIM IS:—

1. A process for the conversion of propylene or isobutylene or a mixture thereof to acrolein and/or methacrolein and/or acrylic acid and/or methacrylic acid, which process comprises contacting propylene and/or isobutylene with molecular oxygen in the presence of a catalyst comprising a composition having the empirical formula:



wherein A is an alkali metal, B is phosphorus and/or arsenic, C is at least one element selected from Group IIA and Group IIB of the Periodic Table, *a* is a number from 0 to less than 0.1, *b* is a number from 0 to 3, *c* is a number from 0.1 to 10, *d* and *e* each is a number from 0.1 to 6, *f* is a number from 8 to 16 and *x* is a number determined by the valence requirements of the elements present other than oxygen, said contacting being carried out in the vapour phase at a temperature of from 500 to 900° F. and at a pressure of from 0.5 to 5 atmospheres.

2. A process as claimed in claim 1 in which the molecular oxygen is supplied in the form of air.

3. A process as claimed in claim 1 in which the molecular oxygen is supplied in the form of molecular oxygen.

4. A process as claimed in any of claims 1 to 3 in which molecular oxygen is supplied in such an amount to provide an oxygen:olefin molar ratio of from 5:1 to 0.5:1.

5. A process as claimed in any of claims 1 to 4 in which the said contacting is carried out in the presence of added water.

6. A process as claimed in any of claims 1 to 5 in which said catalyst comprises support material.

7. A process as claimed in claim 6 in which support material constitutes from 10 to 95 percent by weight of the catalyst.

8. A process as claimed in claim 7 in which the catalyst has been prepared by the steps of:

a) heating a mixture containing support material and components which will provide said composition upon heat-treating, said mixture containing support material in an amount constituting up to 60 percent by weight of the support material which is to be included in the catalyst and said heating being effected at a temperature of from 1000 to 2000° F. in an oxidising atmosphere;

b) reducing the resulting material to a fine powder;

c) mixing the powder with an aqueous slurry of the remaining support material;

d) drying the resulting mixture; and

e) calcining the dried mixture at a temperature of from 750 to 2000° F.

9. A process as claimed in any of claims 1 to 8 in which the element selected from Group IIA and Group IIB is magnesium.

10. A process as claimed in any of claims 1 to 9 which is carried out in a fixed bed reactor, the catalyst being in the form of pellets.

11. A process as claimed in any of claims 1 to 9 carried out in a fluidized bed reactor.

12. A process as claimed in any of claims 1 to 11 including the steps of recovering acrolein and/or methacrolein and/or acrylic acid and/or methacrylic acid.

13. A process as claimed in claim 1 substantially as herein described with reference to Examples 5 to 13 and 15.

14. Acrolein and/or methacrolein and/or acrylic acid and/or methacrylic acid when prepared by a process as claimed in any of claims 1 to 13.

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Reference has been directed in pursuance of Section 9, subsection (1) of the Patents Act 1949, to patents Nos. 1,284,464 and 1,330,074.

